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**GEOCHEMICAL WEATHERING  
OF  
GRANULAR BYPRODUCT MATERIALS**

**By**

**ROBERT K. CARTER  
B.S., University of New Hampshire, 2000**

**THESIS**

**Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of**

**Master of Science**

**in**

**Civil Engineering**

**May, 2008**

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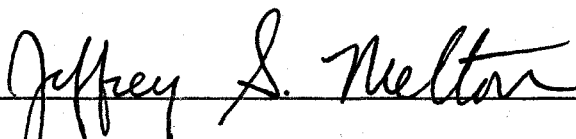
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Thesis Director, Kevin H. Gardner, Associate Professor



Jeffrey Melton, Assistant Research Professor



Jenna Jambeck, Assistant Research Professor

May 9<sup>th</sup>, 2008

Date

## DEDICATION

For My Father who taught me determination,

For my Mother who taught me patience,

For my Wife who gave me love,

For my children who gave me laughter,

And for Kevin, who gave me a chance.

## **ACKNOWLEDGEMENT**

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**ABSTRACT**

**GEOCHEMICAL WEATHERING OF**

**GRANULAR BYRODUCT MATERIALS**

by

Robert K. Carter

University of New Hampshire, May, 2008

Granular byproducts of artificial systems, such as municipal solid waste incinerator ash (MSWI) and coal combustion, are limited in re-use applications because of concern for their long-term environmental behavior with particular focus on the release of heavy metals. Understanding the solid phases within these materials and their influence on heavy metal leaching is necessary for development of an approach to potential re-use applications. Application of traditional geomorphologic principles may describe the solid phases of man-made systems and their development over time. This research addresses identification of the solid phases by use of Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and X-ray Absorption Spectroscopy (XAS) techniques. Four samples of MSW ash and pulverized coal fly ash (PCFA) were used in this research. Results suggest a trend of artificial systems developing similarly to natural systems, and the mineralogical development influencing long term leaching of heavy metals.

## **PART I**

# **GEOCHEMICAL WEATHERING OF GRANULAR BYPRODUCT MATERIALS**

## **Chapter 1**

### **GEOCHEMICAL WEATHERING OF GRANULAR BYPRODUCT MATERIALS**

#### **Introduction**

Incineration of municipal solid waste (MSW) is a key component of waste management strategies in developed countries.<sup>1</sup> This practice results in a volume reduction of the bulk waste material, oxidation of organic materials, recovery of energy, and residuals of inorganic contaminants in both the bottom ash and fly ash from air pollution control devices.<sup>2</sup> Research has shown physical characteristics of ash lend themselves to potential re-use in construction applications.<sup>3</sup> Potential reuse of the resulting bottom and fly ash materials is limited by environmental performance, in particular with respect to leachable heavy metals such as As, Cd, Zn, Pb, Hg, Cu, and Mo.<sup>4,5</sup> In order to better define and quantify the heavy metal leaching characteristics of these ash materials the mechanisms influencing the sequestering and release of the heavy metals must be elucidated.

MSWI bottom ash is composed primarily of amorphous glassy constituents<sup>4</sup> with chemical composition of the coarse fraction including silicate minerals (quartz, gehlenite, plagioclase, etc) and metal oxides ( magnetite, hematite, etc), and the fine fraction containing sulphates (anhydrite, ettringite, etc.) and carbonates

(calcite, siderite).<sup>5</sup> This composition of largely amorphous glass and silicate minerals has resulted in the comparison of MSWI bottom ash to alkaline soils and soils derived from volcanic ash. The geochemical weathering processes observed in these types of soils has been applied to the weathering of MSWI bottom ash.<sup>4, 6</sup> Dissolution and precipitation are the geochemical weathering reactions controlling the leaching of major inorganic mineral soil components.<sup>7, 8</sup> These two weathering processes are equilibrium controlled with respect to the soil solid phase; precipitation during supersaturation conditions of a particular element in the soil solution, dissolution during undersaturation of the soil solution.<sup>7</sup> Heavy metals in bottom ash occur in trace concentrations and the mechanisms controlling their long term leaching characteristics (i.e. decades and longer) are not well understood.

This research studied the mineralogical characteristics of fresh, carbonated, naturally aged, and artificially aged MSWI bottom ash by x-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) to determine weathering products of ash using traditional soil weathering indices. The resulting mineral assemblages were analyzed to determine potential heavy metal inclusion. Leaching experiments as a function of pH were conducted on fresh, carbonated, and aged samples to determine differences in total and available metal concentrations and relationships of leaching properties to weathering processes.

## Literature Review

Physical properties such as size, surface area and charge behavior play an important role in the equilibrium and kinetic reactions in soils<sup>7</sup> and must be well understood in ash particles to determine their influence on leaching of contaminants. Physical properties of ash particles were reviewed by Theis and Gardner (1990) and presented by the International Ash Working Group in "Municipal Solid Waste Incinerator Residues". (Table 1.1)

<b>Table 1.1 - Physical Properties of Ash Particles</b>		
Property	MSW Fly Ash	MSW Bottom Ash
Particle size range, $\mu\text{m}$	0.01-230	295-9500
Specific Surface Area, $\text{m}^2/\text{g}$	2.83-36.93	9.4-46.3
Specific Gravity	2.1-4.04	1.52
Bulk Density $\text{g}/\text{cm}^3$	0.78-1.04	0.37-0.73

Typical pH values for initial pH of bottom ash range from 10.5 to 12.2.<sup>1</sup>

The elemental composition of MSWI bottom ash is influenced by the waste input to the incinerator and the individual operating conditions of the incinerator; specific waste streams may impact the quality of the final residues.<sup>9</sup> However, bulk chemical and elemental composition of fresh bottom ash are generally similar (Table 1.2) with a predominance of amorphous glasses, metals, and salts.<sup>4, 6, 10</sup> The glassy constituents in bottom ash are similar to the composition



of basaltic glasses, an amorphous glassy material in volcanic ash, and as such are potentially unstable in an aqueous environment.<sup>4</sup> In addition, soils derived from volcanic ash, known as Andisols<sup>11</sup>, have a predominance of amorphous or low crystallinity alteration materials<sup>12</sup> as does MSWI bottom ash.<sup>4, 8, 10</sup> Andisols weather rapidly and tend to form amorphous clays such as allophane, imogolite, and ferrihydrite and early stage minerals such as smectites, kaolinite, and vermiculite.<sup>11</sup>

<b>Table 1.2 - Bulk Chemical and Elemental Composition of Fresh MSW Bottom Ash</b>	
<b>Bulk Elemental Composition</b>	<b>Bulk Speciation Composition</b>
Si	SiO <sub>2</sub>
Fe	Fe <sub>2</sub> O <sub>3</sub>
Ca	CaO/ CaSO <sub>4</sub> (2H <sub>2</sub> O)
Al	Al <sub>2</sub> O <sub>3</sub>
Na	Na <sub>2</sub> O/ NaCl
Mg	MgO
K	K <sub>2</sub> O
P	P <sub>2</sub> O <sub>5</sub>
Mn	MnO

Similarities in properties between volcanic ash and MSW bottom ash have enabled the application of geochemical processes known to occur in volcanic ash in predicting the weathering products of MSW bottom ash.<sup>4</sup> In addition, speciation of the major and trace elements in ash materials impacts leaching behavior with the major mineral assemblages often controlling leachate chemistry.<sup>2</sup> The mineral phases determine whether leaching is solubility

controlled (controlled by the solubility of the solid phase), or availability controlled (controlled by under saturation of a particular element).<sup>13</sup>

Leaching of metals such as Cu, Mo, Zn, Pb, and Cd from MSW bottom ash typically decrease as a result of weathering.<sup>8</sup> Sorption processes may control the leaching of these contaminants<sup>8</sup> as amorphous iron and aluminum (hydr)oxides are known to strongly sorb heavy metals,<sup>14</sup> however cation exchange and incorporation into solid phase may also play a role.<sup>15</sup> An understanding of the solid phases of MSW bottom ash is necessary to determine the impact on leaching of potential contaminants.<sup>2, 4, 6, 8, 15</sup> This research attempts identification of the mineralogy and geomorphology of MSW bottom ash and the influence of these on heavy metal leaching.

## **Materials and Methods**

### **Materials**

Samples from four sources were studied during this research: the first sample source was MSWI bottom ash from an experimental lysimeter in Fukuoka, Japan; the second source was MSWI bottom ash from the Nashville Thermal Plant received from Dr. David Kosson and Sarynna Lopez at Vanderbilt University; the third source was pulverized coal fly ash (PCFA) received from Dr. Ole Hjelm of

Vandkvalitetsinstituttet. The fourth sample source was MSWI ash from an experimental lysimeter at the University of New Hampshire.

The sample from Fukuoka, Japan consisted of seven samples, approximately 1,000g each, taken at different depths from a lysimeter exposed to the natural environment of Fukuoka City for three years. The sample depths were 0, 35, 85, 135, 185, 235, and 285 cm.

The samples of MSWI bottom ash received from Dr. David Kosson and Sarynna Lopez at Vanderbilt University consisted of three, approximately 500g sub-samples: ash preserved in a nitrogen atmosphere in initial condition, ash preserved in a nitrogen atmosphere after being aged by exposure to a carbon dioxide-rich atmosphere for one month, and ash preserved in a nitrogen atmosphere after being exposed to atmospheric gas concentrations for one month.

The PCFA received from Dr. Ole Hjelm of the Vandkvalitetsinstituttet, was naturally aged for twenty years in an ash monofill. Four samples of approximately 500 g each, three from depths of the monofill (top, middle and bottom of the approximately 3 meter deep monofill), and one archived sample, were analyzed for comparison.

A fourth MSWI bottom ash sample from a lysimeter in Durham, New Hampshire was used for empirical comparison during defining the procedure used for artificial weathering. This sample had been exposed to the natural environment for ten years. A 500 g composite sample was developed with samples taken from the surface, approximately 35 cm deep and approximately 85 cm deep.

## **Methods**

Prior to analysis, all samples to be analyzed were massed and recorded. Samples were then placed in a 150 ml beaker and dried in an oven set to 50°C  $\pm$  1°C. The mass of the samples was then measured and recorded every twenty-four hours. The sample was considered dry when two subsequent measurements had a difference equal to or less than 0.01g. Dried samples were then pulverized with mortar and pestle and sieved through a #80 (177 $\mu$ m) sieve.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done by combining small amounts of sample (<0.1g) crushed by mortar and pestle with potassium bromide and pressed into a slide. The slides were then analyzed by Colet FTIR Spectroscopy with initial results given in percent transmittance, and comparative results presented in percent absorbance.

For scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS) analysis, two aliquots of each sample were used; each

aliquot was glued to a sample stud with carbon paint. One sample stud was then coated with gold palladium for SEM; the other sample stud was coated with carbon for analysis by EDS. SEM work was done on an Amray 3300 Field Emission S.E.M., and EDS work was done by EDS P.G.T. EDS analysis was for qualitative purposes only.

X-ray diffraction (XRD) work used 1g of each sample divided into three subsamples for triplicate analysis. Approximately 0.3 g of an ash sample was placed on a sample slide and evenly dispersed in the depression of the slide. X-ray diffraction patterns were collected from  $10^\circ$  to  $90^\circ$   $2\theta$ , at a  $0.02^\circ$  step size and residence time of 2.5 seconds/step. Data analysis was performed by Jade software version 5.0 software. Minerals with Figure of Merit (FOM) of 20 or less, as determined by Jade software, were used in analysis of the spectral data.

In X-ray absorption spectroscopy (XAS) samples were pulverized in mortar and pestle, sieved to less than  $100\ \mu\text{m}$  particle size, and mounted on one-sided kapton tape. The tape was folded and placed on the sample holder at the DCM beamline at the Center for Advanced Microstructures and Devices (CAMD) at an energy range of 1-15 keV, and resolution from 0.5 to 2 eV. Empirical standards of calcite, calcite with lead substitution, and aragonite as well as five ash samples were analyzed at both the lead  $L_{III}$  and calcium K edge energies, 13035 eV and 4038.5 eV respectively, for x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS). Data from the lead  $L_{III}$

edge were not used because of the low energy of the CAMD beamlines. Data obtained at the calcium K edge energy was useful and analyzed using Athena/Artemis and WinXas software.

Leaching tests were conducted by mixing ash samples with distilled, de-ionized water at a 10:1 liquid to solid ratio (L:S) using 5 g of ash sample material and 50 ml of distilled, de-ionized water.. The suspensions were then agitated for six hours using a shaker table and filtered through a 0.45  $\mu\text{m}$  filter and preserved. pH dependant leaching was conducted similarly, with the suspensions being maintained at a constant pH for 24 hours.

Artificial weathering of ash samples is defined for the purposes of this report as the method described here. Ash samples of 100 g were placed in a stainless steel encased Teflon pressure vessel at 100% moisture holding capacity as determined by the Standard Method for the Determination of Soil Moisture (oven method). The vessel was sealed using a spring-loaded pressure plate and placed in an oven at 100°C for one month, or 30 calendar days. This method produces mineralogical development similar to that of the composite MSWI bottom ash sample exposed to natural environmental conditions for 10 years and is used as a preliminary indicator of geomorphological behavior of ash materials. Development of a laboratory based artificial aging process is not the focus of the research, but is used as an approximation and empirical comparison.

## Results and Discussion

### FTIR

Spectral data for the Japanese MSWI bottom ash sample taken from 0 cm depth strongly indicate the presence of silicates, carbonates, phosphates and possibly nitrates. Silicates are indicated with diagnostic peaks at  $3450\text{ cm}^{-1}$ ,  $1050$  and  $1100\text{ cm}^{-1}$ ,  $940$ ,  $805$ , and  $450\text{ cm}^{-1}$ .<sup>16</sup> Peaks diagnostic of allophane ( $980$  and  $570\text{ cm}^{-1}$ ), halloysite ( $1100$  and  $470\text{ cm}^{-1}$ ) and possibly immogolite ( $690$  and  $430\text{ cm}^{-1}$ ) are also present representing secondary silicate minerals (Figure 1.1).<sup>17</sup>

Similarly, FTIR spectral data indicated the presence of carbonates, with bands at  $1540$  to  $1410\text{ cm}^{-1}$ ,  $880$  to  $860\text{ cm}^{-1}$ , and approximately  $740\text{ cm}^{-1}$ . Phosphate

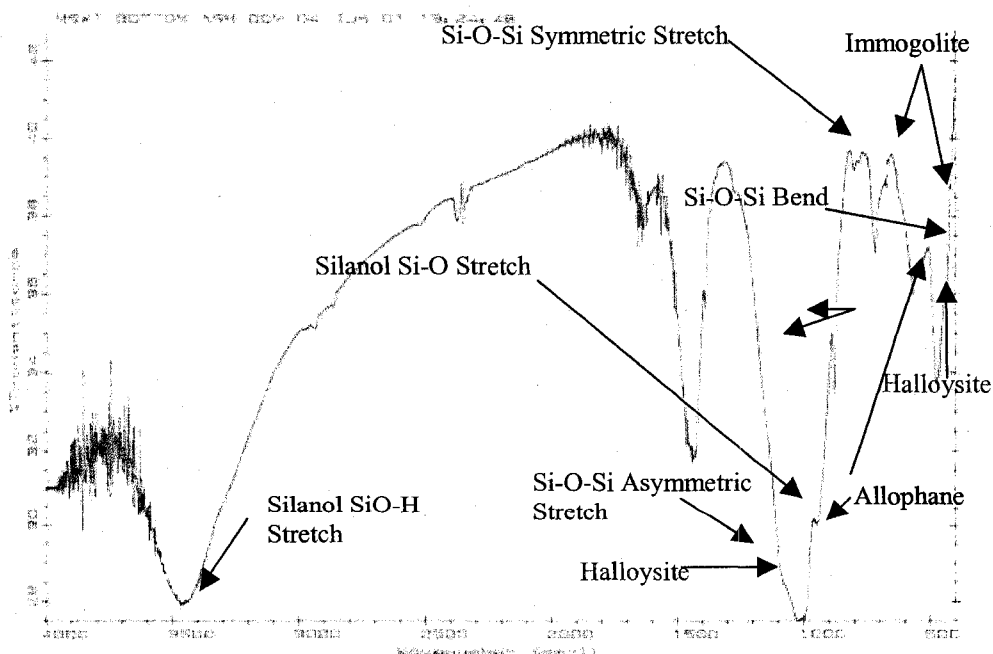


Figure 1.1 - FTIR Spectrograph of MSWI Bottom Ash from a Lysimeter in Fukuoka, Japan - Aged 3 years from 0 cm depth.

bands are pronounced at 1100 to 1000  $\text{cm}^{-1}$ , and at 600 to 500  $\text{cm}^{-1}$ . Nitrate bands are less defined at 1400 to 1340  $\text{cm}^{-1}$ , 840 to 810  $\text{cm}^{-1}$ , and more defined at 720  $\text{cm}^{-1}$ .

FTIR spectral data for the sample from 35 cm (Figure 1.2) show the silanol Si-O stretch is less defined, as well as a decrease in intensity for all silicate peaks. Diagnostic peaks for allophane, imogolite and halloysite are much less intense and less defined than in the surface sample, indicating an overall phase change of the structural form of silica in the sample at 35 cm. Inorganic carbonates and

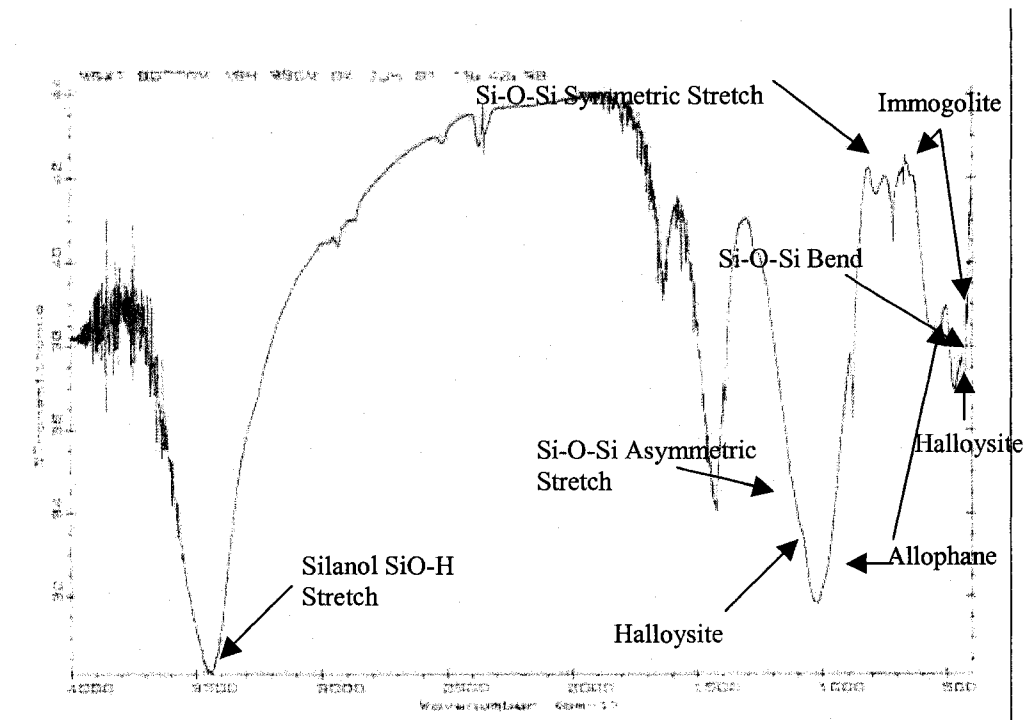


Figure 1.2 - FTIR Spectrograph of MSWI Bottom Ash from Lysimeter in Fukuoka, Japan - aged 3 years, 35 cm depth.



nitrates do not have well defined peaks in the 35 cm sample, lacking a C-O stretch peak, as well as a N-O out of plane bend. This implied decrease is consistent with expected retarded weathering rates with sample at depth considering limited exposure to atmospheric conditions over the three year weathering period. Spectral data for samples from 135 cm and 235 cm show similar trends: a decrease in intensity of diagnostic peaks of carbonates and nitrates, with silicates and phosphates maintaining the most significant presence of mineral structure. The sample from 235 cm shows a slight increase in intensity of peaks of silicates and phosphates, indicative of higher concentrations of relic materials.

Fresh, artificially aged, naturally aged for ten years, and carbonated ash samples were analyzed with resulting spectrographs compared to empirical spectrographs of amorphous clay minerals allophane and halloysite with results given in percent absorbance. (Figure 1.3) The intensity of peaks similar to allophane and halloysite appear to decrease from the fresh ash sample to the naturally aged, artificially aged and carbonated samples. This suggests a phase change in the development of silicate structures in weathering ash materials.

## FTIR Spectroscopy for amorphous clay content

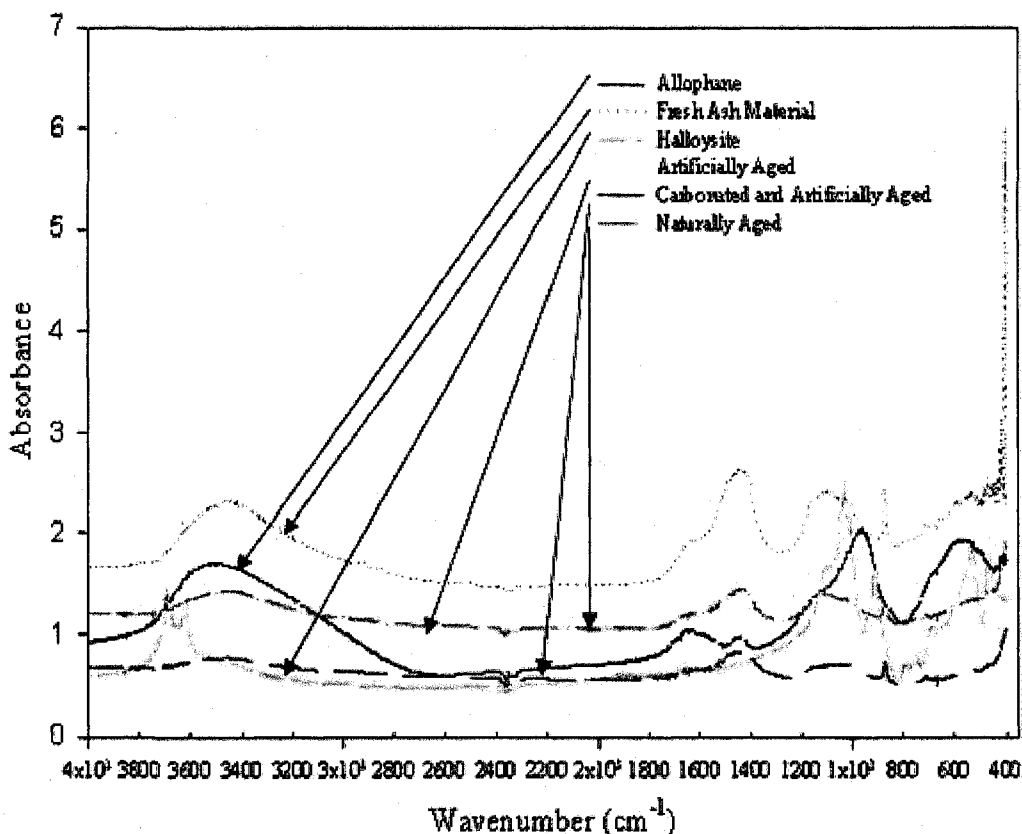


Figure 1.3 – FTIR Spectrograph of samples and empirical standards

## XRD

XRD results for the Japanese samples at 0 cm and 285 cm were compared to develop a weathering profile for the lysimeter samples, with the 285 cm sample analogues to the “parent material”. The major composition of 285 cm sample is quartz, calcite, and gismondine ( $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ ), with minor and trace constituents of metal oxides and hydroxides. The major constituent of the 0 cm sample is calcite, with minor constituents of quartz, metal oxides and hydroxides.

The transition of quartz from a major constituent in the sample at depth to a minor constituent in the surface sample supports the hypothesis of a phase change of the silicate structures. Decrease in aluminum concentrations at the surface where pH values are lower, and aluminum is less soluble, furthers the phase change hypothesis of feldspars transitioning to clay size, amorphous, aluminosilicate minerals allophane and possibly imogolite. Gismondine ( $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9(\text{H}_2\text{O})$ ), a tectosilicate zeolite (framework silicate), is an alteration of plagioclase feldspars.<sup>18</sup> The presence of gismondine in the sample at depth may be relic as zeolites have typically been thought to form from rapid cooling of igneous rock. However zeolites may also occur as alterations of volcanic tuff and glass<sup>19</sup> continuing the analog of MSW ash to volcanic ash. The presence of Gismondine could be explained by the dissolution of Ca at depth where pH values are more basic than at the surface, exposure to  $\text{CO}_2$  is limited, Ca is not bound by carbonate, and is able to be incorporated into silicate mineral structures such as Gismondine. Spectral data obtained from XRD analysis of the fresh, carbonated and artificially weathered ash material demonstrate differences in major compositional content. (Figure 1.4) Figure of merit (FOM) is used in this application as an indicator of peak match when referenced with a tungsten standard for qualitative purposes. Minerals from these samples with FOM of 20 or less are presented in Table 1.3. The intensity of calcite peaks (most notably at  $23.041^\circ$ ,  $29.44^\circ$   $2\theta$ ) is the greatest for the carbonated sample, with relative intensity of 100%, followed by the fresh ash at 87%, and the artificially aged ash at 85%. Quartz (notable at  $20.8^\circ$   $2\theta$ ), which exists as a minor constituent of the

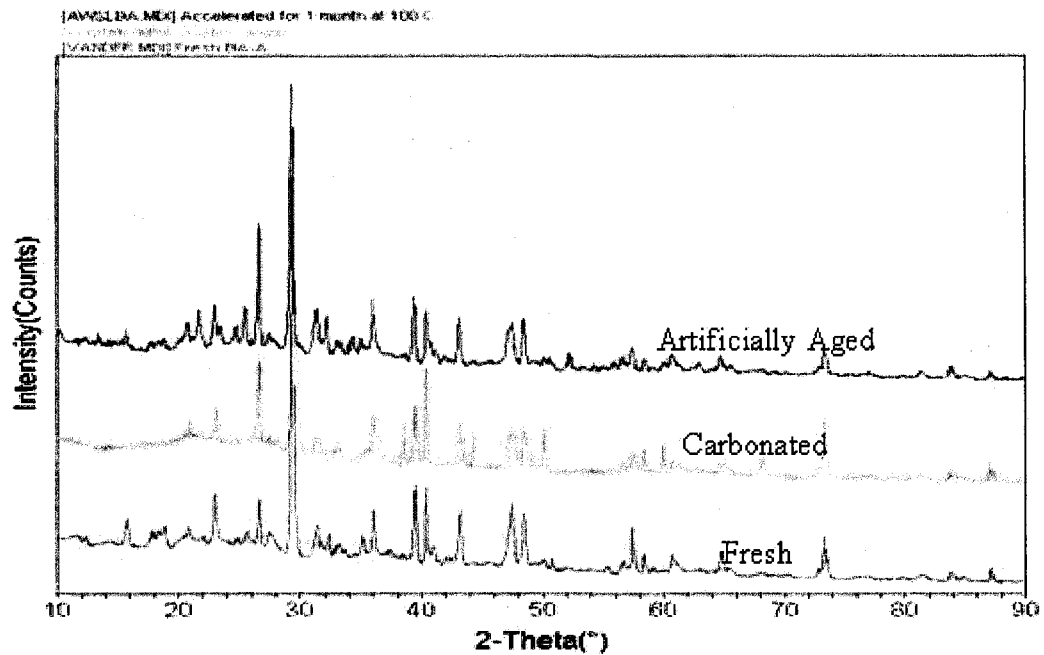


Figure 1.4 - XRD spectrograph of Fresh, Artificially Aged, and Carbonated MSW Bottom Ash Materials

fresh ash material, increases in relative intensity from the carbonated sample at 33%, to the artificially aged sample at 38%.

**Table 1.3 - Minerals with Figure of Merit of 20 or less for Fresh, Carbonated, and Artificially Aged MSWI Bottom Ash Samples**

Sample	Minerals with FOM of 20 or less
Fresh	quartz, Anhydrite, gehlenite, anorthite, iron oxides
Carbonated	quartz, calcite, gehlenite, iron oxides – no hydrate species
Artificially Aged	quartz, ettringite, calcite

With the exception of johannsenite and hedenbergite, both of which are inosilicates, the remainder of the major mineral constituents are sulfides(ates), phosphates, and (hydr)oxides, or variations of these three. Minor constituents of the three samples consist of hydrates and (hydr)oxides of various metals, as well as quartz and calcite. The artificially weathered sample typically has more well defined mineral phases, including alumino-silicate clays, as opposed to the fresh and carbonated ash materials containing less defined metal (hydr)oxides.

XRD spectral data of the three PCFA samples aged naturally for 20 years show only slight differences in mineral composition with depth. (Figure 1.5) The spectral data are presented from top PCFA sample to bottom PCFA sample. Major constituents of the PCFA sample are quartz, calcite, gismondine, and mullite. Gismondine and mullite are typically products of high temperature processes; gismondine, a zeolite is typically found in cavities of igneous rocks, while mullite, a nesosilicate, is typically a ceramic product of high temperature alteration of kaolinite, andalusite, or other anhydrous alumino-silicates. The presence of both these minerals together in the same sample suggests they are relic.

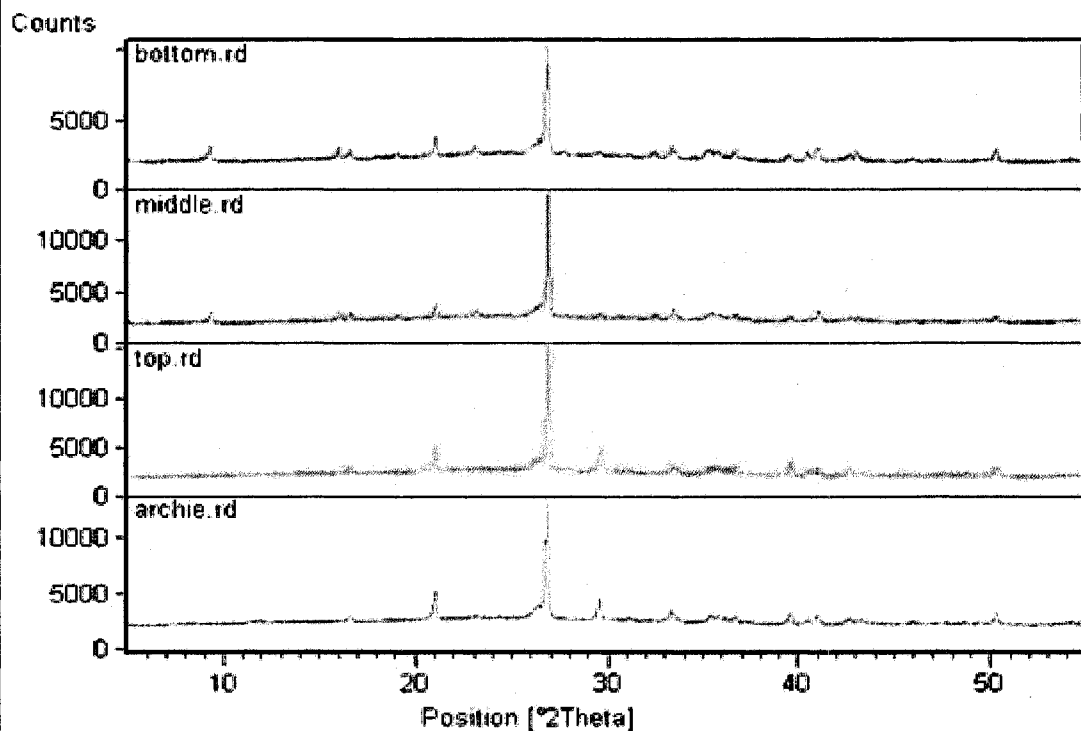
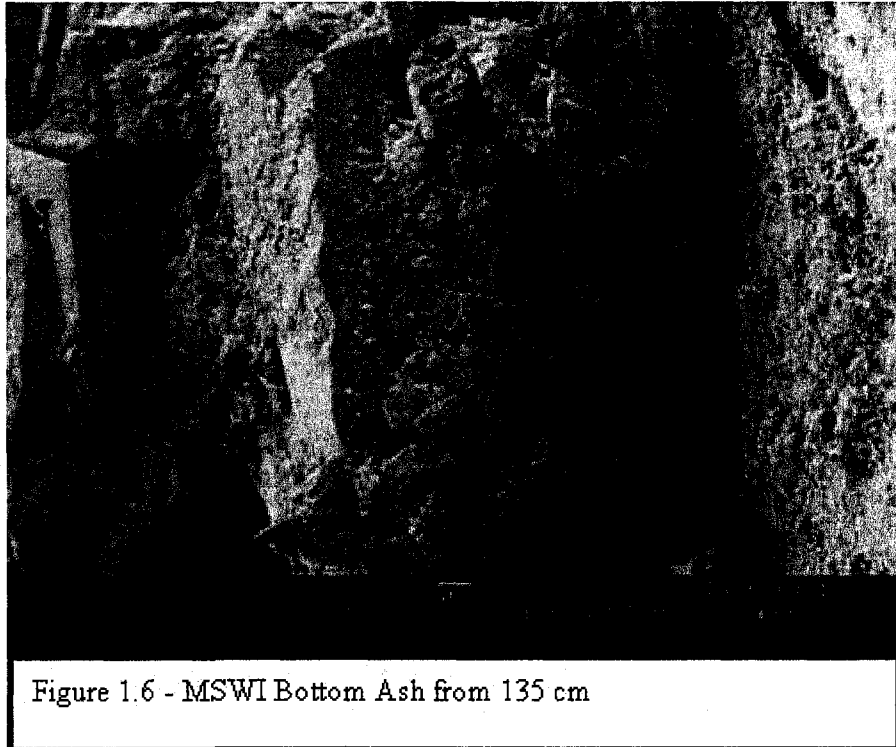


Figure 1.5 - XRD Spectrograph of PCFA ash samples

### **Scanning Electron Microscopy**

SEM micrographs of fresh, artificially weathered, and naturally weathered ash materials present visual indications of the more defined mineral content of the artificially and naturally weathered materials. (Figures 1.6, 1.7 and 1.8) Figure 1.6 at 10  $\mu\text{m}$  resolution, is a three year old ash sample representative of poorly crystalline metal (hydr)oxides. The micrographs in Figures 1.7 and 1.8, artificially aged and 10 year old naturally aged respectively, both at 1  $\mu\text{m}$  resolution, are relatively characteristic of an alumino-silicate clay particle, such as halloysite, a minor constituent of the artificially weathered ash material. This suggests the



method of artificial aging employed is a reasonable facsimile to the natural aging process. EDS qualitative data concurred with the suspected dominant elemental composition of metals, silica, oxygen, and hydrogen.

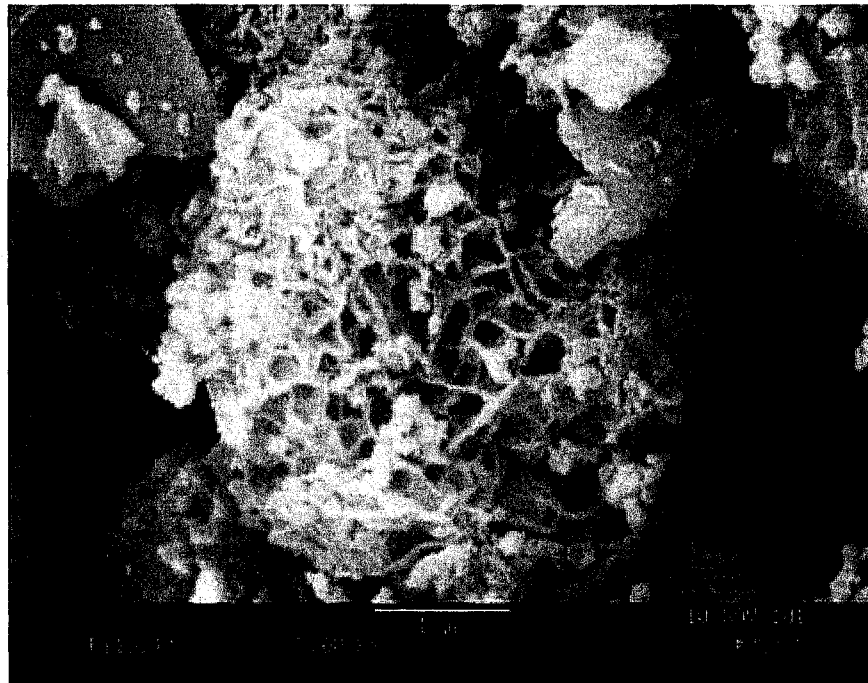


Figure 1.7 - Artificially Aged MSWI Bottom Ash

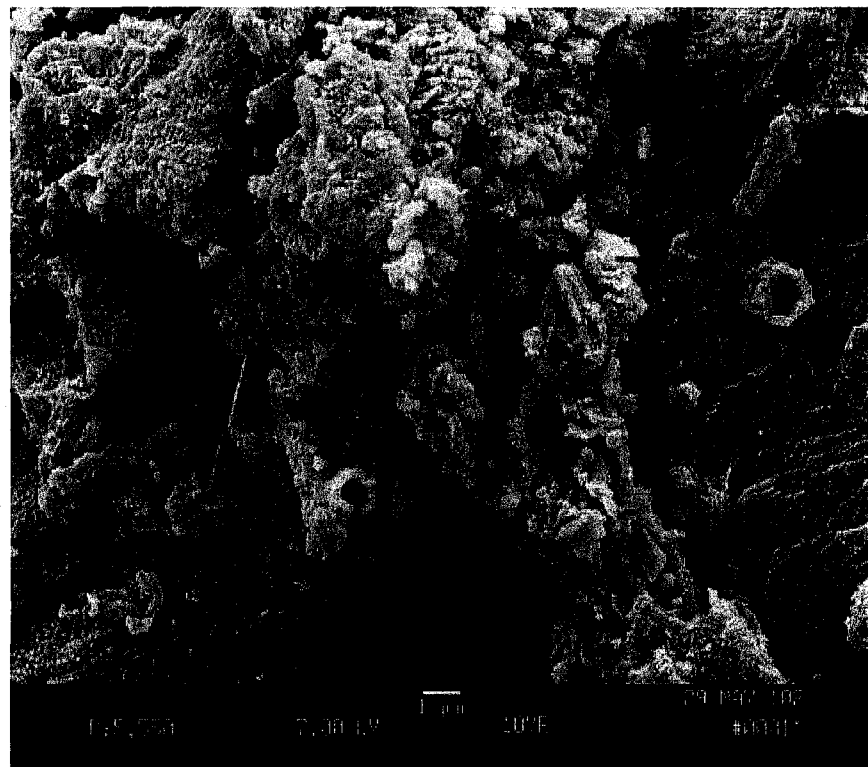


Figure 1.8 - SEM micrograph of 10 year old naturally aged MSWI Bottom Ash



## **X-Ray Absorption Spectroscopy (XAS)**

XANES scans were successfully conducted on all samples except sample 2, artificially aged MSW bottom ash from Japan, (Figure 9), while EXAFS scans were achieved for only the standards and samples 1 and 2 (Figure 10). XANES scans among samples were similar to that of the standard calcite with lead substitution. EXAFS scans demonstrated peak shift with samples when compared to calcite. Carbonated samples tended to have peaks more similar to those of lead substituted calcite. This similarity in XANES scans and shift in EXAFS peaks furthers the hypothesis of the potential for isomorphic substitution of heavy metal ions into precipitating mineral assemblages. In this case, similarities in peaks of samples and the standard of lead substituted in calcite when plotted in "q", or filtered EXAFS data, suggests lead substitution in the calcite structure in the carbonated ash samples.

# Raw XANES Scans of Samples and Standards

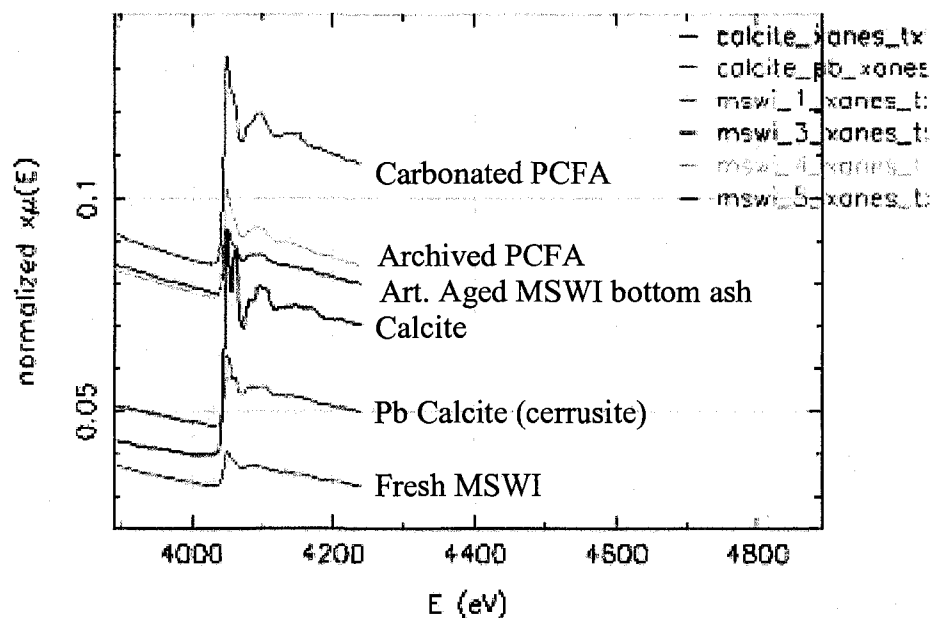


Figure 1.9 - XANES Scans of Standards and Sample 1-Fresh MSWI bottom ash, 3-Art. Aged MSWI bottom ash, 4-archived PCFA, and 5-carbonated PCFA

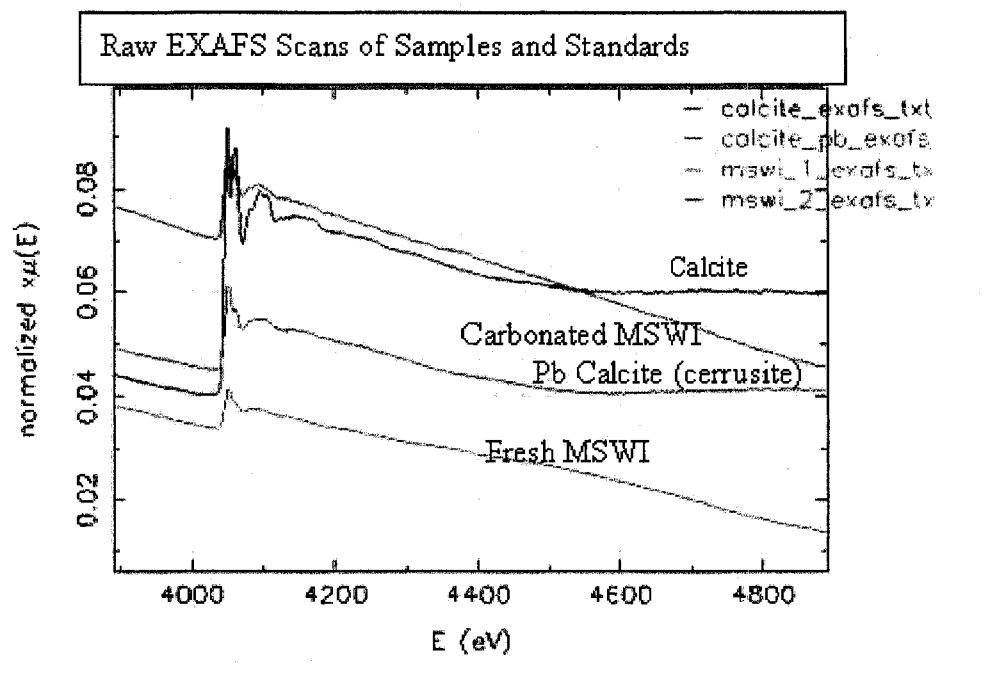


Figure 1.10 - EXAFS Scans of Standards and Samples 1 (Fresh MSWI bottom ash) and Sample 2 (Carbonated MSWI bottom ash)

### **pH Dependant Leaching**

Comparison of lead leachability from fresh ash, carbonated ash, and artificially aged carbonated ash suggests the greatest reduction in available lead in the aged and carbonated samples (Figure 11). pH dependant leaching of mercury and chromium in the pH range of 6 to 10 (Figures 12, and 13 respectively) from artificially aged ash, in general, demonstrate a decreased availability of these metals with age. Leaching of zinc however demonstrates no identifiable trend (Figure 14).

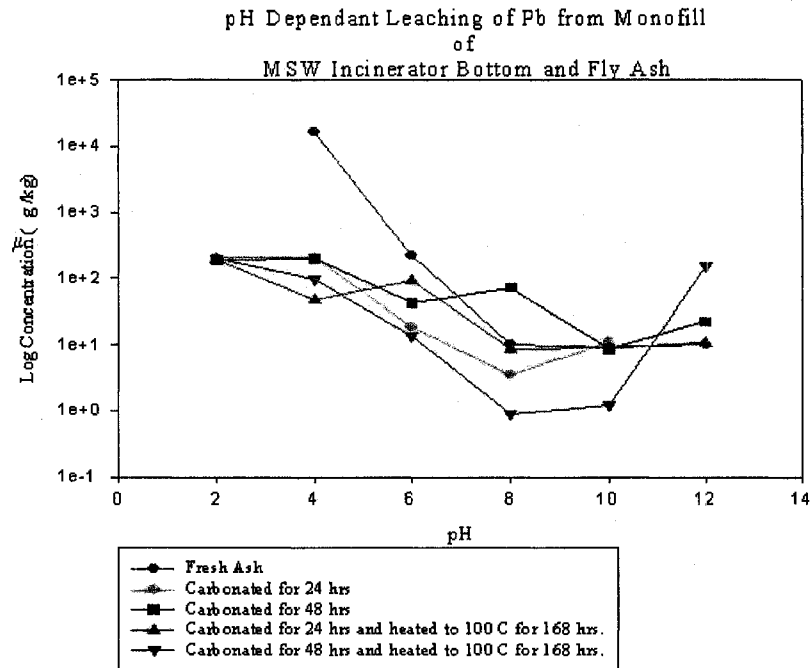


Figure 1.11 – pH Dependant Leaching of Pb from MSWI bottom and fly ash

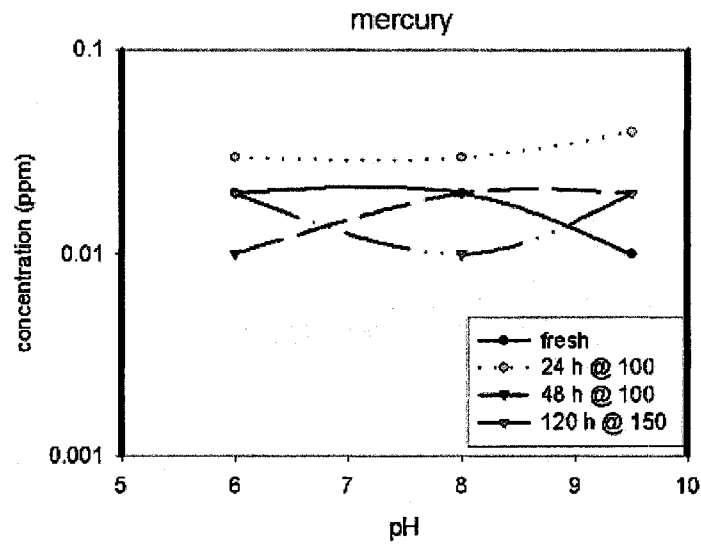


Figure 1.12–pH Dependant Leaching of Hg from Artificially Aged MSW Bottom Ash

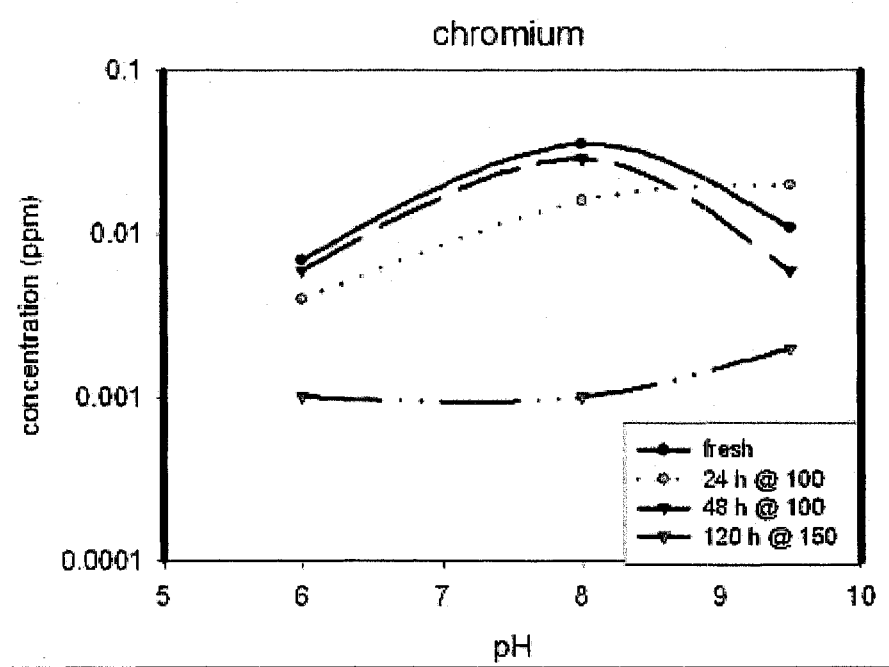


Figure 1.13-pH Dependant Leaching of Cr from Artificially Aged MSW Bottom Ash

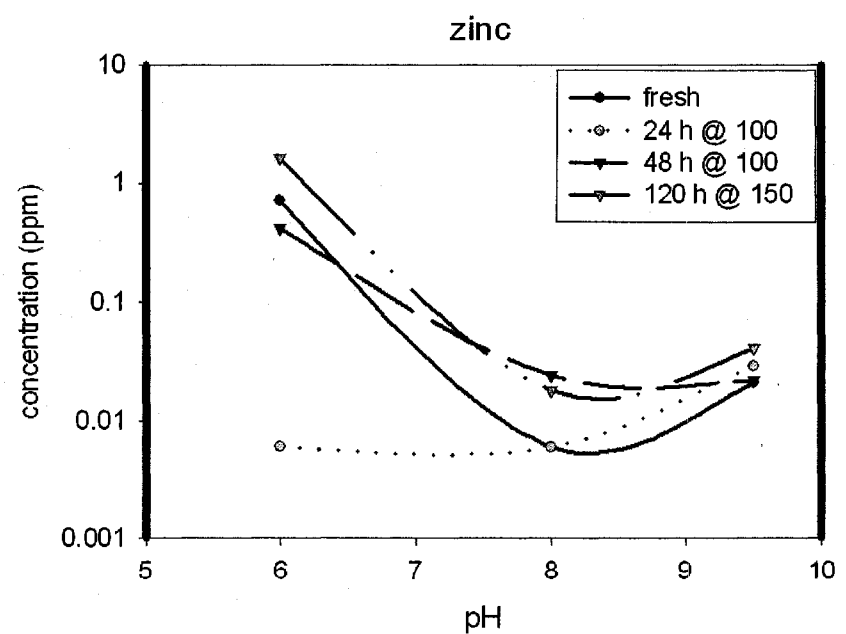


Figure 1.14-pH Dependant Leaching of Zn from Artificially Aged MSW Bottom Ash

## **Conclusion**

The predominance of amorphous mineral assemblages has been confirmed by FTIR, XRD, and SEM results. When viewed in isolation the sample sizes used in the various methods of analysis are not large enough to be deemed representative. However the multiple methods of analysis concurrence of development of mineral and crystalline phase changes suggests the results are representative of actual conditions. Exposure of these materials to natural weathering conditions and processes has shown a progression of geomorphological development with proximity to atmospheric conditions, similar to that of a weathering soil profile. In addition, the mineralogical development of the amorphous constituent of incinerator by-product materials is similar to the progression of volcanic ash to andisols. These developing mineral assemblages have the ability to incorporate heavy metals into their crystalline structure. pH dependant leaching has demonstrated a general decrease in heavy metal availability from the more weathered ash materials, although evidence for this is limited in this study. XAS scans demonstrate a stronger similarity in weathered ash samples to that of lead substituted calcite, suggesting the possibility of lead substitution into the calcite mineral assemblage during its formation, analogous to that occurring in natural systems.

The results of this research suggest that granular byproducts of artificial systems, such as ash generated from MSW incineration and coal combustion, may be

understood more completely by analogy to natural ashes, such as volcanic ash. Consideration of ash monofills as dynamic weathering profiles and incorporation of geomorphologic processes in assessment of long term behavior may result in a more comprehensive understanding of artificial granular byproducts' long term environmental behavior and impact. This greater understanding may lead to a viable and beneficial re-use of these granular products in structural fill applications.

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## PART II

### MECHANISMS FOR REDUCTION OF HEAVY METAL LEACHING BY NATURAL CHEMICAL WEATHERING REACTIONS

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## **Chapter 2**

### **MECHANISMS FOR REDUCTION OF HEAVY METAL LEACHING BY NATURAL CHEMICAL WEATHERING REACTIONS**

#### **Introduction**

There are numerous granular byproduct materials, such as combustion ashes, and smelting and foundry byproduct materials, that are limited in their reuse potential by poor environmental performance. Concern over the leaching of contaminants may result in prohibition against a material's reuse, or may represent an unacceptable liability risk to the corporation, utility, or municipality interested in the reuse of a material. Furthermore, there is a need for greater accuracy in understanding how a material may leach in a given environment over time such that more precise, application-specific exposure scenarios can be developed. A lack of risk information has been cited as one of the largest barriers to the use of recycled materials in highway applications by a recent survey conducted by the Association of State and Territorial Waste Management Officials (ASTSWMO, 2000).<sup>1</sup>

Many granular byproduct materials, however, have been observed to undergo natural transformations when left in an exposed environment for a number of years. These granular materials originate from high temperature processes that produce a byproduct that is thermodynamically unstable in the natural

environment. After chemical weathering of these geochemically unstable “reactants,” the product materials have vastly different environmental properties. These chemical weathering processes have not been well documented in the literature and have only been investigated for a small number of materials from high-temperature processes. Furthermore, mechanisms by which leaching processes are changed by these geochemical reactions have not been elucidated.

This research is focused on further investigation of these natural reactions so that there is a greater understanding of how leaching of contaminants changes with the geochemical weathering of the byproduct material. Furthermore, methods to accelerate the weathering process are being investigated, which offers the potential that beneficiation methods can be used to develop a useful and environmentally acceptable product. Changes in physical properties of these materials will also be investigated to document how the geochemical changes influence the physical and mechanical behavior of the materials, which is an important consideration for the beneficial use of these materials in highway construction.

### **Hypothesis**

Ashes and slags are composed primarily of amorphous minerals, salts, and metals, and meet a non-biological definition of soil as an unconsolidated mineral material.<sup>2</sup> As such, the chemical and physical weathering characteristics of soils can be applied to ash, and the predictions and theories applied to the weathering

of soils may also be applicable. Dissolution and precipitation are chemical weathering processes that impact the inorganic content and composition of unconsolidated mineral materials.<sup>2</sup> Alumino-silicate clay formation is derived from the dissolution of primary minerals and the subsequent precipitation of secondary minerals. The concentrations of aluminum, silicon, other major and minor elements, moisture and the pH of the “soil” solution determine the speciation of the clay mineral formed.<sup>3</sup>

“Surface-controlled” dissolution occurs when transport reactions occur more quickly than surface reactions, which occurs in silicates and oxides. This surface controlled rate is proportional to the surface area of the minerals.<sup>2</sup> Fly ashes are usually fine particles, with relatively large surface areas, while bottom ashes, slags, and foundry and smelting byproducts may be large granular particles with lower surface areas. Volcanic ash has been used as a fly ash and bottom ash analog, as composition, size, and surface area are similar<sup>4, 5</sup> but volcanic ash pH is typically near neutral, while coal and MSWI ashes may have typical pH values from 10 to 13. The relatively large surface area allowing more intense surface controlled dissolution, combined with the difference in “parent material” pH values contribute to the accelerated weathering rate of coal and MSWI ashes. If unaltered coal and MSWI ashes weather rapidly, then the possibility of enhancing and controlling the weathering rate of these ashes is high. Other granular material that is being investigated is not expected to weather at the high rate of very basic fly ashes, although over the long term their weathering and alteration of leaching properties may be significant.

The governing hypothesis for this work is that chemical weathering of industrial byproducts are important to understand in order to predict the long-term environmental impact and risk associated with their beneficial use. Furthermore, it is hypothesized that these chemical reactions can be controlled by manipulating the soil solution conditions, and that they can be accelerated in the laboratory. This research is proceeding by first collecting waste materials that have been exposed to the natural environment for many years. A number of analytical techniques are then being employed to determine an equivalent weathering age, analogous to the weathering stages of soils based on the distributions of primary and weathered products.

## **Materials and Methods**

### **Study Materials**

Although a fair amount of work has been conducted using coal ashes and MSWI bottom ash, these materials are the first materials being studied in this research in order to “calibrate” the methods and aging stages that will be used for these and other materials. The research presented in this paper has been conducted on MSWI bottom ash mined from a lysimeter in Japan. MSWI bottom ash was placed in this lysimeter for a period of three years, and was left exposed to the environment in the city of Fukuoka, on the southern-most island of Japan. The lysimeter was sampled after 3 years and samples were taken from 7 depths -

sample 1 – 0 cm, sample 2 – 35 cm, sample 3 - 85 cm, sample 4 – 135 cm, sample 5 – 185 cm, sample 6 – 235cm, and sample 7 - 285 cm.

### **Experimental Methods**

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done by combining small amounts of sample (< 0.1g) crushed by mortar and pestle with potassium bromide and pressing into a slide. The slides were then analyzed by Colet FTIR Spectroscopy with results given in percent transmittance.

Two sets of samples were glued to a sample stud with carbon paint. One sample stud was coated with gold palladium for scanning electron microscopy (SEM). The other sample stud was coated with carbon for analysis by energy dispersive x-ray spectroscopy (EDS). SEM work was done on an Amray 3300 F.E. S.E.M., and EDS work was done by EDS P.G.T. EDS analysis was qualitative only, not quantitative.

For x-ray diffraction (XRD) work, 1g of each sample to be analyzed was crushed by mortar and pestle and sieved through a number 50 sieve (300  $\mu\text{m}$ ). Approximately 0.3g of the sample were placed on a slide without altering the surface of the sample, and placed in the slide tube. Data analysis was performed by Jade software version 5.0 software.

Leaching tests were conducted by mixing ash samples (crushed and sieved to <200  $\mu\text{m}$ ) in distilled, deionized water in a 10:1 liquid:solid ratio (5 g solid in 50 ml solution). The suspension was agitated for 6 hours and filtered through a 0.45

$\mu\text{m}$  filter and preserved as appropriate for chemical analysis. pH-dependent leaching was carried out in a similar fashion, maintaining a pH-stat condition at different pH values with the use of strong acid and strong base.

Post analysis of the initial materials, 15 g of sample 1 was subjected to 185 ° C under 100% saturation, for 96 hours, then analyzed by SEM and XRD to determine degree of crystallinity and effectiveness of hydrothermal treatment as method for acceleration of weathering reactions.

## **Results and Discussion**

Previous research on MSWI Bottom Ash has determined the main crystalline phases to be silicates, oxides, carbonates, and salts.<sup>6</sup> Our analysis of MSWI Bottom Ash aged for three years in a lysimeter, by FTIR, SEM, EDS, and XRD, shows preliminary results concurring with these findings.

Fourier Transform Infrared Spectroscopy (FTIR) has been used to monitor phase change in solids of contaminated weathering soils, though not widely used in analysis of ash materials.<sup>7</sup> Utilizing this approach to view solid phase change of naturally weathering amorphous ash materials will assist in defining the depth and extent of the weathering front, and rate of pedochemical and geochemical processes.

Spectral data for sample 1 (0 cm depth) strongly indicate the presence of silicates, carbonates, phosphates and possibly nitrates. Silicates are indicated with diagnostic peaks at  $3450\text{ cm}^{-1}$ ,  $1050$  and  $1100\text{ cm}^{-1}$ ,  $940$ ,  $805$ , and  $450\text{ cm}^{-1}$



<sup>1,8</sup> Peaks diagnostic of allophane (980 and 570  $\text{cm}^{-1}$ ), halloysite (1100 and 470  $\text{cm}^{-1}$ ) and possibly immogolite (690 and 430  $\text{cm}^{-1}$ ) are also present representing silicate minerals (Figure 2.1).<sup>7</sup> Similarly, FTIR spectral data indicated the presence of carbonates, with bands at 1540 to 1410  $\text{cm}^{-1}$ , 880 to 860  $\text{cm}^{-1}$ , and approximately 740  $\text{cm}^{-1}$ . Phosphate bands are pronounced at 1100 to 1000  $\text{cm}^{-1}$ , and at 600 to 500  $\text{cm}^{-1}$ . Nitrate bands are less defined at 1400 to 1340  $\text{cm}^{-1}$ , 840 to 810  $\text{cm}^{-1}$ , and slightly more defined at 720  $\text{cm}^{-1}$ .<sup>8</sup>

FTIR spectral data for sample 2 at 35 cm showed the silanol Si-O stretch is less defined, as well as a decrease in intensity for all silicate peaks. Diagnostic peaks for allophane, immogolite and halloysite are much less intense and less defined than in sample 1, indicating an overall phase change of the structural form of silica. Inorganic carbonates and nitrates do not have well defined peaks in sample 2 lacking a C-O stretch peak, as well as a N-O out of plane bend. This implied decrease is consistent with expected retarded weathering rates with sample at depth considering limited exposure to atmospheric conditions.

Spectral data for samples 3 and 4, 135 cm and 235 cm, respectively, showed similar trends: a decrease in intensity of diagnostic peaks of carbonates and nitrates, with silicates and phosphates maintaining the most significant presence of mineral structure. Sample 4 shows a slight increase in intensity of peaks of silicates and phosphates, indicative of higher concentrations of relic materials.

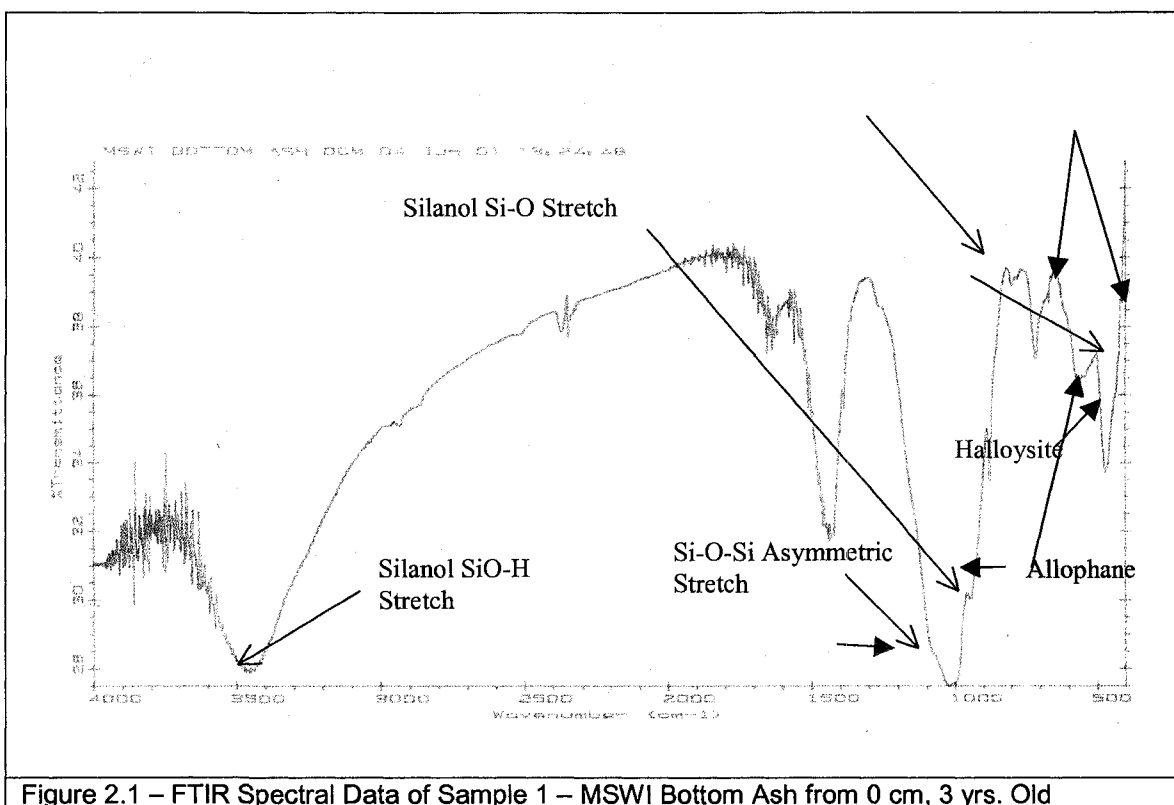
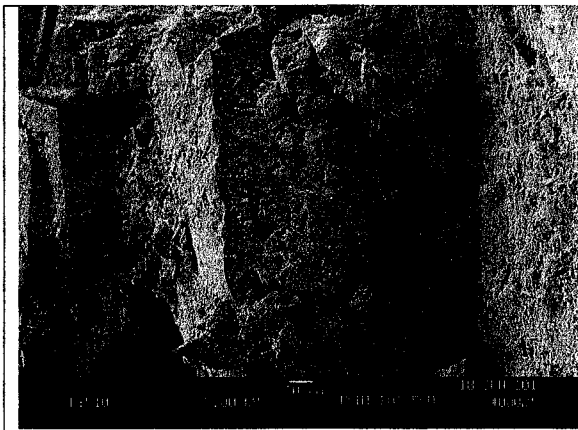


Figure 2.1 – FTIR Spectral Data of Sample 1 – MSWI Bottom Ash from 0 cm, 3 yrs. Old

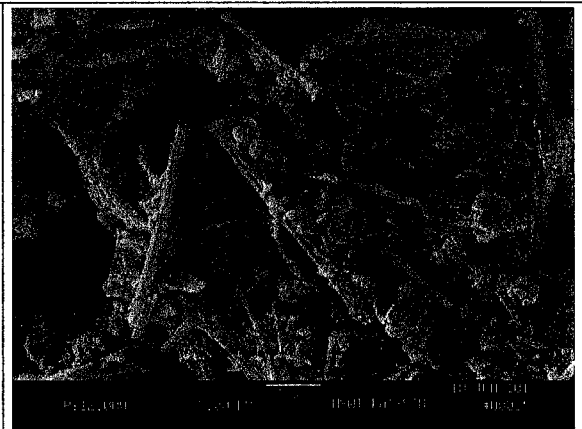
SEM micrographs of fresh and hydrothermally treated ash materials (Figures 2.2 through 2.5) show a phase change in the mineral structure resulting from the hydrothermal treatment. Micrographs 2.4 and 2.5 are characteristic of clay like particles.

EDS determination of chemical composition by atomic percentage indicates the presence of Al, C, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, O, P, Pb, S, Si, Ti, and Zn. XRD results for samples 1 and 7, 0 cm and 285 cm, respectively, were reviewed for a comparison to view the lysimeter samples as a weathering profile, with sample 7 analogues to the “parent material”. The major composition of sample 7 is quartz, calcite, and gismondine ( $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ ), with minor and trace

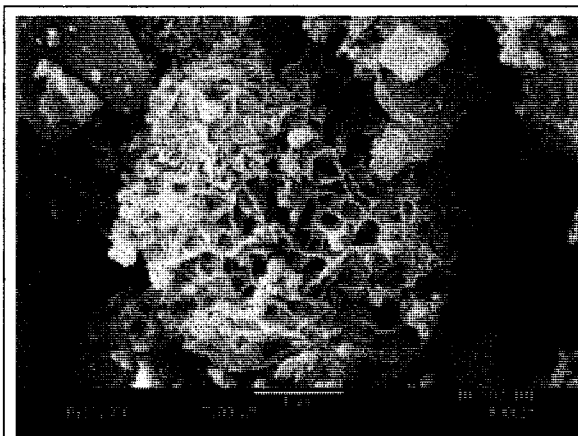
constituents of metal oxides and hydroxides. The major constituent of sample 1 is calcite, with minor constituents of quartz, metal oxides and hydroxides.



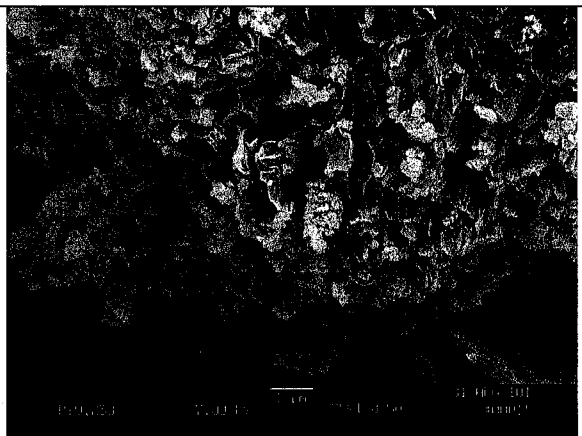
2.2-SEM of ash material aged for 3 yrs.



2.3-SEM of ash material aged for 3 yrs.



2.4 - Ash subjected to 48 hours at 100°C



2.5 - Ash subjected to 96 hours at 185°C

Gismondine ( $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9(\text{H}_2\text{O})$ ), a tectosilicate zeolite (framework silicate), is an alteration of plagioclase feldspars.<sup>9</sup> The presence of gismondine in the sample at depth is likely relic as zeolites have typically been thought to form from rapid cooling of igneous rock. However zeolites may also occur as alterations of volcanic tuff and glass;<sup>10</sup> application of this theory to the glassy constituent of

bottom ash allows the hypothesis of natural geochemical processes occurring. In the sample at depth, where pH values are more basic than at the surface, and exposure to CO<sub>2</sub> is limited, Ca is not bound by carbonate, and is able to be incorporated into silicate mineral structures.

Cation exchange capacity (CEC) and pH dependant leaching of Pb data support the development of alumino-silicate clay materials as well. CEC of the 0 cm sample is substantially higher than the subordinate samples, despite the smaller specific surface area. These factors may explain the drastic difference in Pb leachability at the higher (>10) pH levels.

XRD results for samples subjected to hydrothermal treatment indicated the presence of quartz, tridymite, anorthite, albite, calcium oxide as primary constituents. Anorthite, CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, and albite, NaAlSi<sub>3</sub>O<sub>8</sub>, are plagioclase feldspars, while tridymite is part of the silicate group, ideally SiO<sub>2</sub>, with possible incorporation of Na and Al.

### **Conclusion**

The presence of allophane and immogolite, and their pedogenic subordinate halloysite, in three year old MSWI bottom ash leads to the hypothesis that alumino-silicate clay minerals will develop from the natural weathering of these ashes. The indication by FTIR analysis of phase changes at depth allows for

determination of a weathering or pedogenic profile to be established. With the profile established, and the species of crystalline structures present within each profile, an approximate age may be applied to form a reference for leaching characteristics of materials at varying degrees of geochemical alteration. The weathering of allophane and immogolite to halloysite, as opposed to gibbsite or kaolinite, implies a limiting factor in the weathering process. If these factors, pH, ionic concentrations, moisture, and temperature, are controlled in attempts to accelerate the weathering process, the speciation of the resulting alumino-silicate clay may be controlled. The positive results from hydrothermal treatment of the formation of plagioclase feldspars strongly concurs with the hypothesis of accelerating the weathering processes by manipulating the factors involved in the weathering process. This not only has implications for future conduct of research on these materials, but for potential long-term treatment methods as well.

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### **PART III**

#### **MINERALOGICAL AND LEACHING CHARACTERISTICS OF WEATHERED INDUSTRIAL ASH**

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### **Chapter 3**

## **MINERALOGICAL AND LEACHING CHARACTERISTICS OF WEATHERED INDUSTRIAL ASH**

### **Introduction**

Incinerator byproduct materials, both fly and bottom ash, are composed primarily of amorphous minerals, salts, and metals, and meet a non-biological definition of soil as an unconsolidated mineral material.<sup>1</sup> As such, the chemical and physical weathering characteristics of soils can be applied to ash, with the predictions and theories applied to the weathering of soils also applicable to these granular byproduct materials. Dissolution and precipitation are chemical weathering processes that impact the inorganic content and composition of unconsolidated mineral materials.<sup>2</sup> Dissolution of the soluble components of amorphous ash material and their subsequent precipitation leads to a crystalline mineral development in aging ashes, with maturation of the ash determinable by the speciation of crystalline mineral composition. Identifying the speciation and development of crystalline minerals with maturation of the ash will contribute to understanding the controlling mechanisms in their heavy metal leaching characteristics. To better understand the natural impact of natural weathering on ash materials a natural analog is used to assess the natural weathering progression and degree of mineralogical development of these industrial granular byproduct materials.



Volcanic ash has been used as a coal fly ash and bottom ash analog, as composition, size, and surface area are similar.<sup>3</sup> However volcanic ash pH is typically near neutral, while coal and MSWI ashes may have typical pH values from 10 to 13. Differences in pH aside, the weathering products of volcanic ash material will be similar in long term mineralogical and physical properties. The relatively large surface area of the ash materials permits more intense surface controlled dissolution than typical soils. This combined with the difference in initial pH values contribute to the natural rapid weathering rate of coal and MSWI ashes. Since unaltered coal and MSWI ashes weather rapidly, the possibility of enhancing and controlling the weathering rate of these ashes is high. The artificial accelerated weathering of ash materials in a laboratory setting allows for elucidation of the controlling mechanisms in heavy metal leaching properties.

The governing hypothesis for this work is that chemical weathering of industrial byproducts are important to understand in order to predict the long-term environmental impact and risk associated with their beneficial use. Furthermore, it is hypothesized that these chemical reactions can be controlled by monitoring and altering the variables in soil solution conditions, and that the reactions can be accelerated in the laboratory. This research has progressed by collecting ash materials preserved in initial condition and comparing the mineralogical development of the fresh materials to that of naturally aged materials of similar or identical origin. The fresh ash materials are then subjected to accelerated weathering techniques with resultant relative age of this artificially weathered material determined by comparison to mineralogical and crystalline speciation

and development of naturally aged materials. A number of analytical techniques are being employed to determine an equivalent weathering age, analogous to the weathering stages of soils based on the distributions of primary and weathered products.

## **Materials and Methods**

### **Sample Materials**

Three sub-samples of municipal solid waste incinerator bottom ash (MSWI bottom ash) were received from Dr. David Kosson and Sarynna Lopez at Vanderbilt University: ash preserved in a nitrogen atmosphere in initial condition, ash preserved in a nitrogen atmosphere aged by carbonation for one month, and ash preserved in a nitrogen atmosphere naturally aged for one month.

Pulverized coal fly ash (PCFA) was received from Dr. Ole Hjelmar of the Vandkvalitetsinstituttet, naturally aged for twenty years in an ash monofill.<sup>4</sup>

Samples from three depths of the monofill (top, middle and bottom of an approximately 3 meter deep monofill) were analyzed for comparison. Although not of identical origin, similarities in both particle size and chemical composition of the MSWI bottom ash and PCFA sample materials allow for a limited comparison as to potential development of the younger ash material.

## **Experimental Design**

The high temperature thermal processes involved in incineration are analogues to the high temperature processes involved in a volcanic event which results in formation of ash materials. These high temperature processes produce a byproduct that is thermodynamically unstable in the natural environment. After subsequent chemical weathering of these geochemically unstable reactants, the product materials have vastly different environmental properties. To examine the geomorphological development of the weathering ash and characterize this development as a function of time, analysis of the amorphous species, elemental composition, and crystalline phases of the fresh and aged ash materials must be determined.

Carbonation of granular byproduct materials, MSW incinerator bottom ash in particular, has been shown to reduce certain heavy metal leaching characteristics as well as the pH of the subjected material.<sup>5</sup> The mineralogical development of the ash influenced by carbonation has yet to be well defined. Accelerated weathering by elevated temperature and pressure at 100% moisture holding capacity, potentially in conjunction with carbonation, would mimic the major chemical weathering conditions of naturally weathered mineral materials. Variables in the conditions that allow an acceleration of natural weathering without yielding products that would not occur in a natural weathering environment must be manipulated to best replicate an equivalent end product.

X-ray powder diffraction has been utilized to analyze crystalline mineral phases of fresh ash material, carbonated material, artificially accelerated weathered material, combined carbonated and artificially accelerated weathered material, as well as various naturally aged ash materials. Samples were ground by mortar and pestle, then sieved through a number 80 (177 micron opening) sieve. X-ray diffraction patterns were collected from  $10^\circ$  to  $90^\circ$   $2\theta$ , at a  $.02^\circ$  step size and residence time of 2.5 seconds/step. The resultant diffraction patterns of these materials have then been compared. Scanning electron microscopy (SEM) has been used to visually validate the presence of the crystal mineral phases identified by XRD. Samples sieved through a number 80 sieve were mounted on a carbon coated (adhesive) sample stud then coated with gold palladium. Leaching characteristics of the carbonated material and combined carbonated and artificially weathered material were identified by batch pH dependant leaching tests, in the pH range of 2 to 12.

### **Results and Discussion**

Spectral data obtained from XRD analysis of the fresh, carbonated and artificially weathered ash material demonstrate differences in major compositional content. (Figure 3.1) Mineral components of each ash sample with figure of merits (FOM) less than 20, as calculated by Jade Software version 5.0 software used for interpretation of the spectral data are given in Table 3.1.

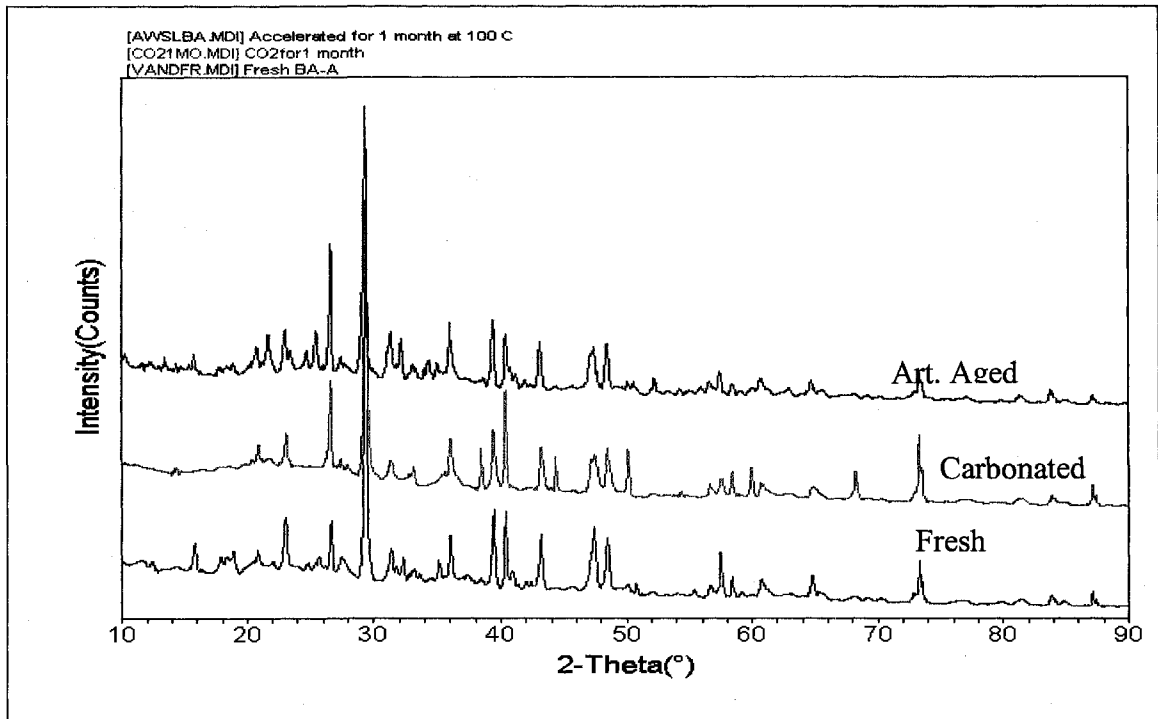


Figure 3.1 – XRD Spectral data of MSWI bottom ash – (top = artificially aged, middle = carbonated, bottom = fresh bottom ash)

Figure of merit is used in this application as an indicator of peak match when referenced with a tungsten standard for qualitative purposes. The intensity of calcite peaks (most notably at 23.041, 29.44  $2\theta$ ) is the greatest for the carbonated sample, with relative intensity of 100%, followed by the fresh ash at 87%, and the artificially aged ash at 85%. Quartz (notable at 20.8  $2\theta$ ) which only exists as a minor constituent of the fresh ash material, increases in relative intensity from the carbonated sample at 33%, to the artificially aged sample at 38%. With the exception of johannsenite and hedenbergite, both of which are inosilicates, the remainder of the major mineral constituents are sulfides(ates), phosphates, and (hydr)oxides, or variations of these three.

Table 3.1 – Mineral Composition of Ash Materials with Figure of Merit < 20			
Sample Source	Mineral Name	Chemical Formula/Mineral Group	Figure of Merit
Fresh Ash Material	Calcite, syn	CaCO <sub>3</sub> /Carbonate	4.9
	Cobalt Phosphate	Co <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> )/Phosphate	9.8
	Piypite	K <sub>2</sub> Cu <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub> /Anyhydrous Sulfate	10.4
	Hedenbergite	CaFeSi <sub>2</sub> O <sub>6</sub> /Inosilicate	11.7
	Billingsleyite, syn	Ag <sub>7</sub> AsS <sub>6</sub> /Sulfide-sulfosalt	12.7
	Brandtite	Ca <sub>2</sub> Mn(AsO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O/Hydrated Phosphate	12.7
	Silicon Sulfide	SiS <sub>2</sub> /sulfide	17.5
Carbonated Material	Calcite, syn	CaCO <sub>3</sub> /Carbonate	4.5
	Calcium Cobalt Vanadium Oxide	CaCoV <sub>2</sub> O <sub>7</sub> /Oxide	7.8
	Silicon Sulfide	SiS <sub>2</sub> /Sulfide	7.8
	Magnesium Vanadium Oxide	MgV <sub>2</sub> O <sub>6</sub> /Oxide	9.6
	Billingsleyite, syn	Ag <sub>7</sub> AsS <sub>6</sub> /Sulfide-sulfosalt	10.2
	Piypite	K <sub>2</sub> Cu <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub> /Anyhydrous Sulfate	10.7
	Johannsenite	CaMnSi <sub>2</sub> O <sub>6</sub> /Inosilicate	10.7
	Quartz, syn	SiO <sub>2</sub> /Silicate	12
	Brandtite	Ca <sub>2</sub> Mn(AsO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O/Hydrated Phosphate	14.2
Artificially Weathered Material	Calcite, syn	CaCO <sub>3</sub> /Carbonate	3.7
	Calcium Cobalt Vanadium Oxide	CaCoV <sub>2</sub> O <sub>7</sub> /Oxide	4.2
	Zinc Hydroxide	Zn(OH) <sub>2</sub> /Hydroxide	15.6
	Ammonium Calcium Sulfate	(NH <sub>4</sub> ) <sub>2</sub> Ca <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /Sulfate	15.6
	Burtite, syn	CaSn(OH) <sub>6</sub> /Hydroxide	15.6
	Sodium Zinc Phosphate	NaZn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> /Phosphate	16.1
	Sodium Iron Selenite	NaFe(SeO <sub>3</sub> ) <sub>2</sub> /Selenite	17.4
	Magnesium Phosphate	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> /Phosphate	18.6
	Potassium Sodium Manganese Oxide	K <sub>2</sub> NaMnO <sub>4</sub> /Oxide	18.9
	Quartz, syn	SiO <sub>2</sub> /Silicate	18.9

Minor constituents of the three samples consist of hydrates and (hydr)oxides of various metals, as well as quartz and calcite. The artificially weathered sample typically has better defined mineral phases, including alumino-silicate clays, as opposed to the fresh and carbonated ash materials containing more poorly defined metal (hydr)oxides.

XRD spectral data of the three PCFA samples aged naturally for 20 years show only slight differences in mineral composition with depth. (Figure 3.2) The

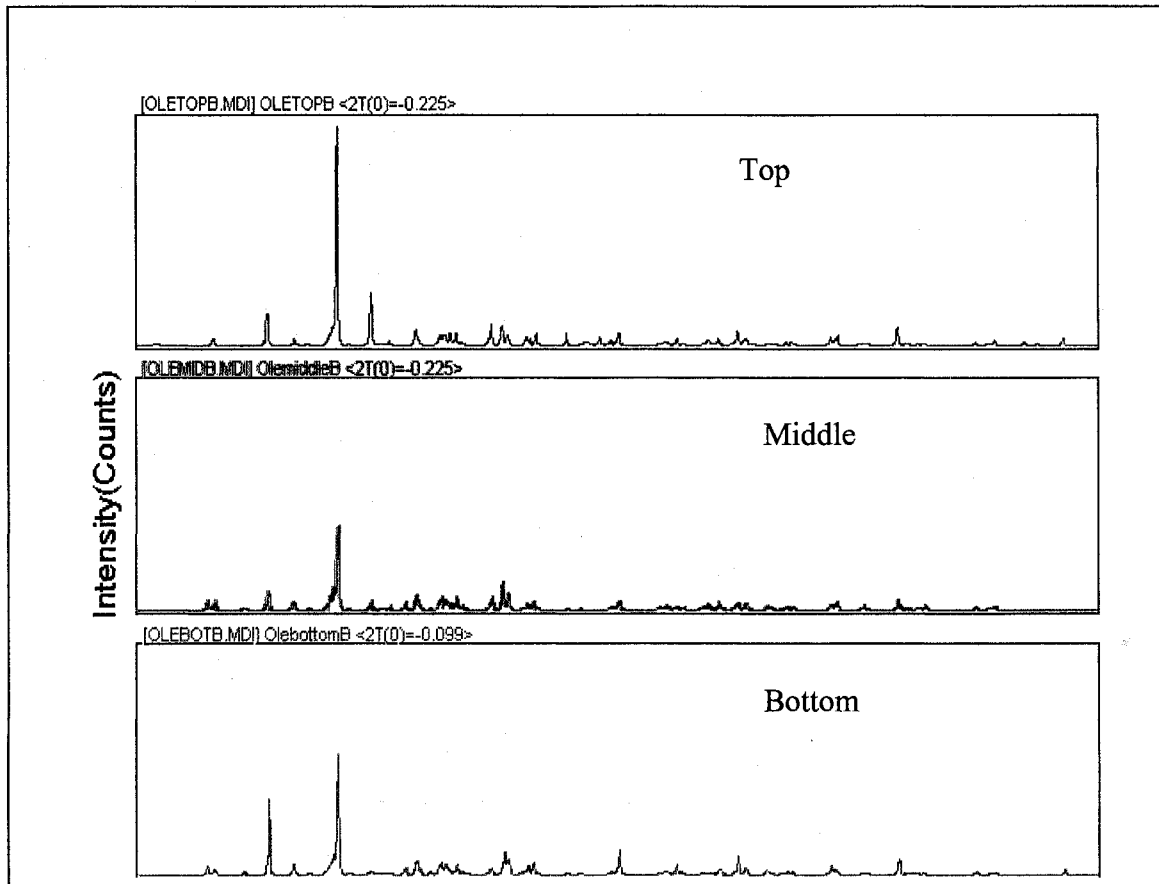


Figure 3.2 – XRD spectral data of PCFA aged 20 years  
spectral data are presented from top PCFA sample to bottom PCFA sample.

Major constituents of the PCFA sample are quartz, calcite, gismondine, and mullite. Gismondine and mullite are typically products of high temperature processes; gismondine, a zeolite is typically found in cavities of igneous rocks, while mullite, a nesosilicate, is typically a ceramic product of high temperature alteration of kaolinite, andalusite, or other anhydrous alumino-silicates. It is possible the presence of these minerals is relic of the original material, or may be a natural weathering progression of initial ash components.

SEM micrographs of carbonated, artificially weathered, and naturally weathered ash materials present visual indications of the more defined mineral content of the artificially and naturally weathered materials. (Figures 3.3, 3.4 and 3.5)

Figure 3.3 is representative of poorly crystalline metal (hydr)oxides.

The micrographs in Figures 3.4 and 3.5 are relatively characteristic of an alumino-silicate clay particle, such as halloysite, a minor constituent of the artificially weathered ash material.

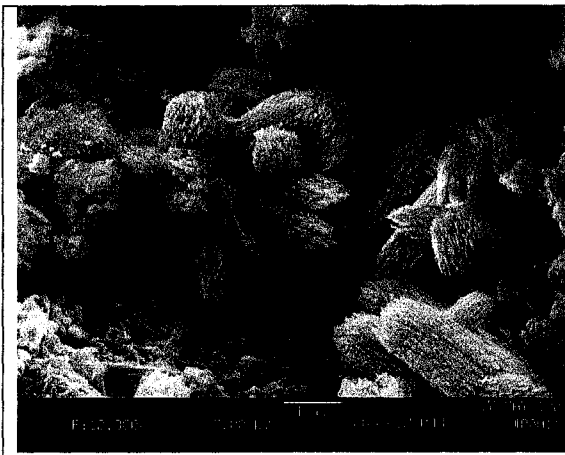


Figure 3.3 – SEM micrograph of carbonated ash

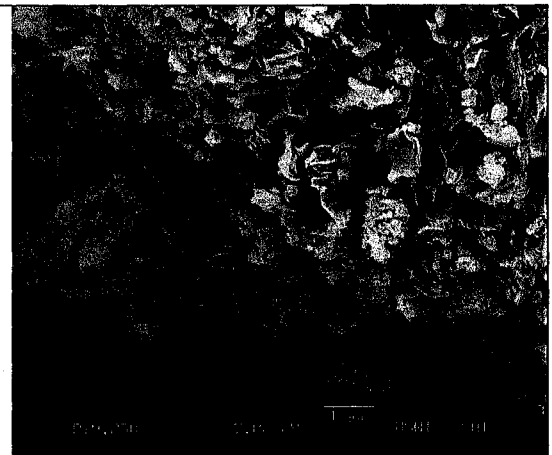


Figure 3.4 – SEM micrograph of artificially weathered ash

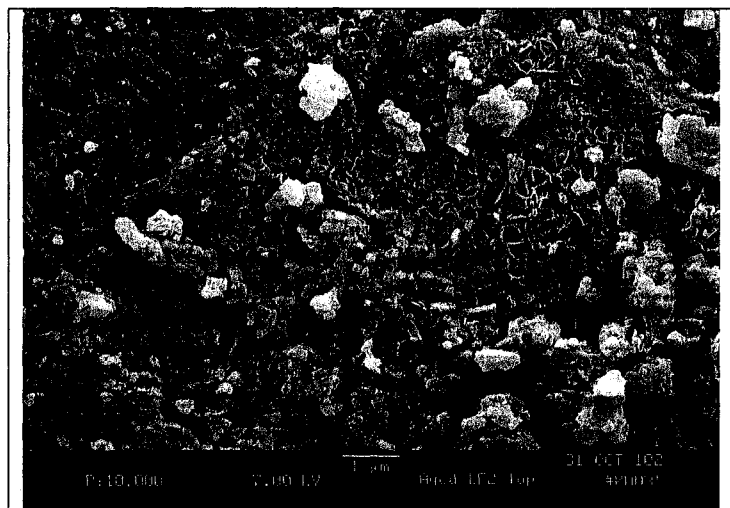


Figure 3.5 – SEM micrograph of PCFA aged 20 years+



The micrographs, in conjunction with XRD results, suggests the method of artificial weathering being used as acceptable in developing mineral phases that would occur under natural weathering conditions.

The implications of the weathering on lead leaching characteristics of the MSWI bottom ash were determined by pH dependant leaching tests. (Figure 3.6) The combined artificial weathering and carbonation has the greatest reduction in lead leaching in the range of 2 to approximately 10.

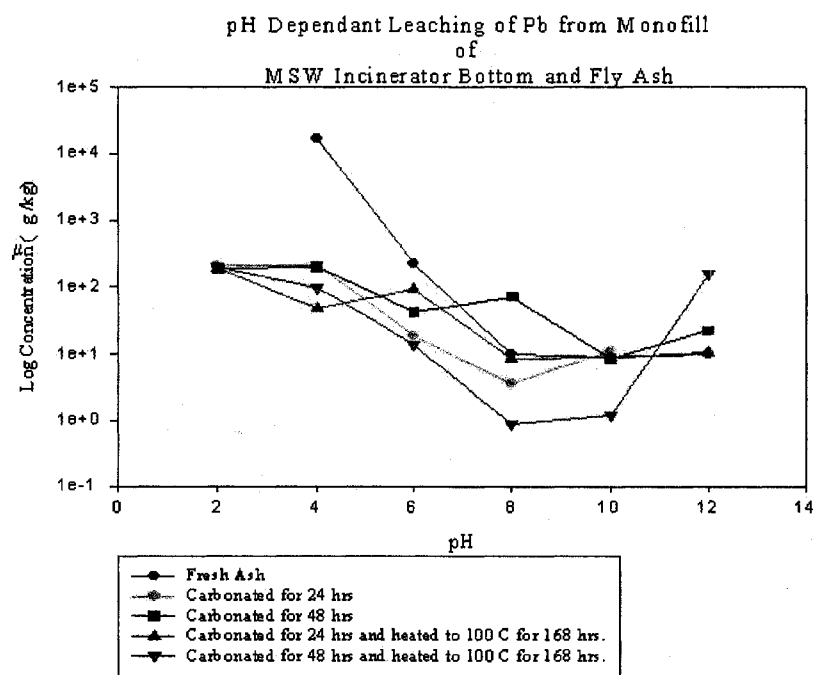


Figure 3.6 – pH Dependant Leaching of Pb from MSWI bottom and fly ash

## **Conclusion**

The development of a potential beneficial re-use of industrial byproduct materials is imperative. In order to ensure an environmentally stable product, better understanding of the entire morphological maturation process of these materials must be attained. The artificial weathering by elevated temperatures and pressures provides a practical and controllable means by which to evaluate the geomorphological development of incinerator residues, with potential application to a wide variety of industrial granular byproducts. In addition, by studying the crystalline mineral composition and phases of development, our knowledge of the long term leaching behavior and subsequent environmental stability will be better refined. The tendency for weathering ash materials to develop toward alumino-silicate materials is consistent with the use of volcanic ash as a natural analog, and consistent with observations of naturally weathered incinerator residues.

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